Theoretical and experimental study of imine-enamine tautomerism of condensation products of propanal with 4-aminobenzoic acid in ethanol

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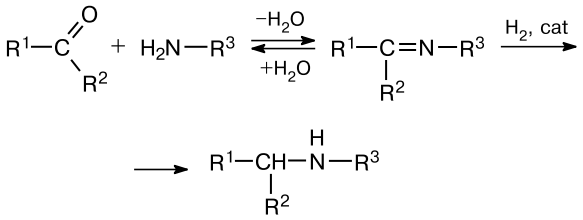
The tautomerism of the reaction products of propanal with 4-aminobenzoic acid in ethanol was studied by J-modulated spin-echo (JMOD) ^{13}C NMR spectroscopy and gradient-enhanced heteronuclear (ge-2D) $^{1}H—^{13}C$ HSQC spectroscopy. The existence of imine and enamine tautomeric forms of the reduced compounds in solution was established. The tautomeric equilibrium of the condensation product of propanal with 4-aminobenzoic acid in ethanol was found to be shifted toward the imine form. Quantum chemical calculations by the density functional theory (DFT) method demonstrated that the 4-(*N*-propylidene)aminobenzoic acid molecule forms a stronger hydrogen bond with an ethanol solvent molecule compared to the enamine molecule, resulting in a higher stability of the ethanol adduct of azomethine compared to the adduct of enamine.

Key words: hydrogenation amination, Schiff bases, imine-enamine tautomerism, density functional theory, NMR spectroscopy, ge-2D HSQC, JMOD.

Systems based on carbon nanomaterials (carbon nanotubes, carbon nanofibers, nanodiamonds (ND), graphene-like nanomaterials, *etc.*) containing transition metals are of interest for application in chemical and pharmaceutical industry. These systems exhibit high catalytic activity for hydrogenation of unsaturated organic compounds containing various functional groups.[1]

The liquid-phase reductive amination (Scheme 1) is a green chemistry method, which is applied as a one-pot procedure for the synthesis of structurally different secondary and tertiary amines.[2]

Scheme 1



cat is a catalyst.
R^1, R^2, R^3 are alkyl, aryl, or aryl heterocycles.

Previously, we have demonstrated that this reaction can proceed under mild conditions (ethanol or propan-2-ol as the solvent, $T = 318$ K, $P(H_2) = 0.1$ MPa) in the presence of different catalysts based on platinum- and palladium-containing carbon nanomaterials.[1] In the present work, the hydrogenation amination of aldehydes with primary amines was investigated. We studied the reductive amination of propanal with 4-aminobenzoic acid under mild conditions ($T = 318$ K, $P(H_2) = 0.1$ MPa, ethanol) in the presence of a palladium-containing carbon nanomaterial based on ethylenediamine-functionalized graphite oxide as a model reaction. Quantum chemical calculations were performed for the molecules of the reduced compounds. The correlations responsible for characteristic groups of atoms were studied by gradient-enhanced 2D heteronuclear correlation (ge-2D $^{1}H—^{13}C$ HSQC) NMR spectroscopy in order to prove the existence of imine-enamine tautomerism in solution and confirm the chemical structure of the compound produced by hydrogenation.

Experimental

Methods of investigation. The hydrogenation amination products were analyzed by NMR spectroscopy. The samples were

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 0070—0075, January, 2017.
1066-5285/17/6601-0070